

**A7 - Indexing, Software****A7 - O1****INDEXING WITH THE SUCCESSIVE DICHOTOMY METHOD, DICVOL04****D. Louër¹ and A. Boultif²**

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Ab initio powder pattern indexing is required in many applications of the powder method, such as *ab initio* structure determination from powder X-ray diffraction data. The objective of pattern indexing is to reconstruct the 3-dimensional reciprocal lattice from the radial distribution of *d*-spacings in the diffraction pattern. In practice, the methodology consists in finding the crystal data of the material, i.e. the dimensions of the unit cell and lattice symmetry. Among approaches reported for pattern indexing, the efficiency of the successive dichotomy method introduced by Louër and Louër [1] has been proved by many years usage. The method is based on the variation, in parameter space, of the lengths of cell edges and inter-axial angles by finite ranges, which are progressively reduced according to a dichotomy algorithm. The absolute error on peak measurements is incorporated in the procedure, without any re-evaluation during the numerical calculations. Solutions are then searched exhaustively in an *n*-dimensional space, from *n* = 1 (cubic lattice) to *n* = 6 (triclinic lattice). The method strategy is based on the search of solutions with smallest cell volumes. Data precision is a major factor of successful indexing and the de Wolff figure of merit acts as solution filter. The development of the computer program, using the dichotomy principle, has been carried out by stages according to the progresses of computing technology over forty years. The most recent program DICVOL91 [2] has been used for indexing hundreds of powder diffraction patterns, from which subsequent structure determinations were often carried out. Although the selection of the input parameters offers strategy choices to the user, indexing practices have revealed the need for new options.

The new facilities implemented in DICVOL04 [3] include (i) a tolerance for unindexed diffraction lines, (ii) the

refinement of the 'zero-point' shift, (iii) an *a priori* analysis of input data to detect the presence of significant zero-point error, (iv) the use of the reduced cell concept to identify equivalent solutions in monoclinic and triclinic systems and (v) a reviewing of all available peak positions from the unit cell parameters found from, generally, the first twenty lines (if no dominant zone is present). Additionally, different strategies have also been applied, particularly to reduce the risk to miss a solution because of metric lattice singularity. Default values have been adapted to more convenient parameters according to the data precision available with high resolution powder diffractometers.

DICVOL04 has been tested with many powder data sets, most of them found in literature, e.g. in the NBS Monograph No. 25, the 71 data sets of Section 20 and all triclinic examples reported in the entire Monograph, powder data of pharmaceutical compounds collected with the capillary technique and monochromatic X-rays, and difficult cases reported in recent publications. The benefit of zero-shift refinement and *a priori* evaluation of zero-error for *in situ* powder data has been shown. The success rate of DICVOL04 is high. Nevertheless, it should be reminded that data quality remains a major requirement. This is due to the nature of the mathematical problem which involves the restoration of a 3-dimensional object from 1-dimensional data.

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A7 - O2

INDEXING POWDER PATTERNS FROM MIXED SAMPLES USING JOINT-PROBABILITY HEURISTICS: HMAP AND PEURIST

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The ab initio lattice reconstruction and unit cell determination for single-component powder diffraction data is already a difficult computational problem, even for well-corrected data with only six unknown cell parameters [1], so it is not surprising that even quite small numbers of impurity lines can make indexing uncertain. A second unknown major phase brings a further six parameters, so that the prospects of successfully indexing mixed samples are generally regarded as poor, despite recent progress using global optimisation programs like McMaille [2] and AUTOX [3].

Apart from the computational demands of searching the resulting greatly enlarged solution space, a major problem is the poor ability of the usual indexing figures of merit (FOM) like M20, M1 and FN to identify solutions in the presence of extraneous lines. All such FOM are based on the discrepancies between observed and calculated lines. They work well when all observed lines are explained by the model, but the signal from a correct cell is easily lost in the large noise term from even a few unindexed lines. A traditional answer is to exclude “unindexed” lines from the FOM calculation, but this just introduces new problems, through making wrong cells appear to have good FOM by excluding their worst discrepancies.

This property of reporting overall misfit rather than fit prevents traditional discrepancy-based FOM from performing well when the model is incomplete, which also limits their usefulness for parameter-separation heuristics, which can greatly speed computations by avoiding the need to search many unknown parameters concurrently.

These disadvantages would disappear for FOM that reported the amount of fit between data and model, while being broadly transparent to any remaining misfit. Such properties are offered by a joint-probability approach like

the PM measure originally proposed by Ishida and Watanabe [4]. PM itself is not well behaved mathematically, due to arbitrary discontinuities, but the present study will report new better-behaved measures – in particular Ir, which reports the “indexedness” of a pattern for a particular trial cell, as a non-integral effective number of indexed lines.

Tests using the new program Hmap running under the latest release of the Crysfire system [5] have shown that Ir has the desired property of being relatively transparent to unexplained lines, routinely disregarding 10 or more impurity lines. It will be demonstrated that in non-pathological cases there are now reasonable hopes of indexing all the components of mixtures of two and sometimes three unknown low-symmetry phases, even with only (good) laboratory data. Hmap is not able to perform full ab initio indexing unaided, since it requires a 4-parameter SIW basis set obtained, for example, with a program like Lzon [5]. This limitation will be removed in a new program Peurist, currently under development, which will carry out full ab initio indexing using joint probability criteria at all stages. Progress with Hmap and Peurist will be reported and demonstrated.

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A7 - O3**TOTAL PATTERN ANALYSIS USING PF-4 RELATIONAL DATABASES****John Faber***International Centre for Diffraction Data (ICDD), Newtown Square, PA 19073, USA*

The fundamental underpinnings for qualitative and quantitative phase analysis have rested with the description of diffraction results in terms of a concise peak-list, i.e., d-spacing/peak intensity pairs. These are taken from the experimental data, usually after background subtraction and alpha-2 stripping. However, there are obvious shortcomings in this approach. Information details concerning background variations, amorphous components in the scattering pattern and peak-width information have been purposefully removed from consideration (e.g. stress/strain). However, the effects of the instrumental resolution function and peak broadening persist.

In this paper, we will follow these historical developments and show qualitatively how Bragg peak resolution affects the quality of pattern matching using Smith-Snyder FOM criteria[1]:

$$F_N = \frac{1}{|2|N_{\text{poss}}},$$

where N is the number of observed Bragg reflections, is the average error, and is the number of possible reflections. Specifically, we will use calculated patterns obtained from the ICDD PDF-4 databases and show how symmetry and peak breadth affect the FOM. Residuals derived from unit cell least-squares analyses also correlate with these observations.

In contrast, we will examine methods for Total Pattern Analyses as implemented in DDView+, the front-end software in the PDF-4 relational databases [2-3]. We will explore how TPA helps us to recover search-indexing details that have been overlooked or lost using data reduction methods. Along the way, we will review several current developments in total pattern matching techniques.

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A7 - O4**BRASS 2004, THE BREMEN RIETVELD ANALYSIS AND STRUCTURE SUITE****J. Birkenstock, R. X. Fischer, T. Messner***Fachbereich Geowissenschaften, Universität Bremen, Klagenfurter Straße, D-28359 Bremen, Germany*

BRASS consists of a suite of programs for the refinement, presentation, and evaluation of crystal structures. Its Rietveld kernel is based on the PC-Rietveld plus program [1], a derivative of the Wiles & Young code [2]. Latest extensions are the implementation of a grid search analysis as introduced in [3], the introduction of an extended version of the modified Pseudo-Voigt profile function according to [4], the handling of peak broadening due to anisotropic strain [5], and beam-overflow intensity corrections for circular sample surfaces [6].

The user interface, written in Delphi, handles the complete file management and data transfer between all modules in *BRASS*. Directories and file structures for input and output, and for the individual program modules are set up upon starting a new project. The user is guided through the Rietveld run by consecutive steps from the powder pattern display to the refinement procedure and the display of the results. Single refinement results can be stored before subsequent runs are performed. A report documenting the ac-

tions is written to a log file. The refinement progress is monitored displaying the residuals and divergence criteria in online graphics. All individual parameter changes are recorded for retrospective analyses.

Quantitative phase analyses can be performed on up to 15 crystalline phases. Results are given in mole percent and weight percent for the individual phases and are displayed in a pie chart. In addition a sum formula is calculated for the bulk composition of the whole sample.

The numerical part of the Fourier calculations is based on the *FORDAP* program [7] extended by comprehensive graphics for the 2D and 3D representation of electron densities and grid search results displaying occupancies and residuals in layers of the unit cell.

The structure drawing part of the program package based on the old version of the *STRUPLO* program [8] is completely rewritten for the online display of polyhedral representations or ball and stick models. All single objects (atoms, bonds, polyhedra) can be deleted by mouse clicks



on the respective objects. A comprehensive redo option allows the recovery of all or just individual objects.

Interatomic distances and angles are listed in a table for all atoms, or they can be displayed online for individual atoms selected by mouse clicks in the graphics display. The void space, i.e., the empty space not occupied by atoms, is calculated according to the procedure described in [9]. This is especially useful to determine diffusion paths, e.g., in porous materials like zeolites.

The program package can be downloaded free of charge from www.brass.uni-bremen.de.

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A7 - O5

POWDER3D, AN EASY TO USE PROGRAM FOR DATA REDUCTION AND GRAPHICAL PRESENTATION OF LARGE NUMBERS OF POWDER DIFFRACTION PATTERNS

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One of the major advantages of powder diffraction compared to other analysing techniques is to (indirectly) measure changes of the entire crystal structure as a function of time, pressure, temperature, chemical composition, magnetic field etc.

Once online image plate readers and high resolution CCD cameras became available, they shall force changes in methods of data analysis and presentation. Typical read-out times are now on the order of seconds. Soon, milliseconds will become standard, producing huge amounts of data which need to be processed in a reasonable amount of time.

The new software solution presented here aims to provide a tool for just this purpose. At the present time the implemented functionalities include data reduction for Rietveld refinement and powerful graphical representations of 2D and 3D powder diffraction data in presentation quality (see figures showing the phase transformations and decomposition of $\text{Rb}_2\text{C}_2\text{O}_4$ which is subject of another abstract). The software design and functionality has been optimised to allow a substantial amount of automation if desired by the user.



